

Synthesis and Fluorescence of *alt*-Copoly[1, 4-divinylenebenzene/1, 4-bis(dimethylsilylene)benzene]

Xiao Bang DUAN¹, Guo Ping CAI¹, William P. WEBER², Ping LU^{1*}

¹Department of Chemistry, Zhejiang University, Hangzhou 310027

²K. B. and D. P. Loker Hydrocarbon Research Institute, Department of Chemistry,
University of Southern California, Los Angeles, CA 90089-1661, USA

Abstract: Silicon inserted π conjugated copolymer was synthesized by Heck reaction with moderate molecular weight. This silicon containing copolymer is thermally stable to 400 °C, while emission of this polymer is blue-shifted compared with polyphenylenevinylene greenish emission. It shows potential application as organic emitter in OLED.

Keywords: Silicon containing polymer, Heck reaction, photoluminescence.

There is considerable interest in thin-film organic electroluminescent devices. *alt*-Copoly (phenylene/vinylene)s have been extensively investigated due to their efficient photoluminescence which can be tuned from blue-green to orange-red. At present, there is a need for materials that emit in the blue region of the visible spectrum¹. Recently several monomeric model systems² and low molecular weight *alt*-copolymers that contain phenylene, vinylene and silylene units have been reported. The silylene units interrupt the direct π -conjugation that causes these materials to fluorescence in the blue region³. Silylene groups that separate two conjugated moieties can also facilitate intramolecular photoinduced charge transfer processes⁴ and may improve polymer processability.

Such polymers have been prepared in several ways. For example, low molecular weight copolymers have been prepared by Wittig reactions between appropriate *bis*-ylids and aromatic dialdehydes⁵, or by Heck reactions between suitable aromatic halides and vinyl compounds⁶. Alternatively, they have been prepared by chloroplatinic acid catalyzed hydro-silylation reactions, for example, between 1, 4-diethynylbenzene and diphenylsilane⁷. Successful hydrosilylation polymerizations have also been carried out with tris(triphenyl)rhodium chloride or iodide catalysts⁸⁻¹⁰. Recently, acyclic diene metathesis (ADMET) polymerization of 1, 4-bis(vinyldimethylsilyl)benzene by various ruthenium complexes has

* E-mail: Pinglu@zju.edu.cn

provided an alternative route to *alt*-copoly[1, 4-bis(dimethylsilylene) benzene/vinylene]¹¹.

We would like to report an alternative synthetic approach to such materials, based on palladium acetate/tri-*o*-tolylphosphine catalyzed Heck reaction of dibromo-aromatic compounds with¹², for example, 1, 4-bis(vinyldimethylsilyl)benzene in the presence of a stoichiometric amount of triethylamine (**Figure 1**). In this reaction, Si-C bonds are formed and hydrobromic acid is lost. The molecular weight of the *alt*-copolymers obtained is modest but comparable to those previously reported¹³. Trace amount of terminal vinyl groups were detected by ¹H NMR. Heavy atom quenching by terminal aryl bromine atoms is not a problem (**Figure 2**). The *alt*-copolymer is easy to cure by hydrosilylation of the terminal vinyl groups which undergo hydrosilylation more easily than the internal vinyl groups.

In comparison, *alt*-copoly[1, 3-divinylenebenzene/1, 4-bis(dimethylsilylene)-benzene] ($M_w/M_n = 2100/1800$) was also achieved by the reaction of 1, 4-bis(vinyldimethylsilyl)benzene with 1, 3-diiodobenzene under the same reaction condition. The fluorescence spectrum shows that the resulting *alt*-copolymer has a shorter emission wavelength (**Figure 3**).

Figure 1 Preparation of *alt*-copoly[1, 4-divinylenebenzene/1, 4-bis(dimethylsilylene)benzene]

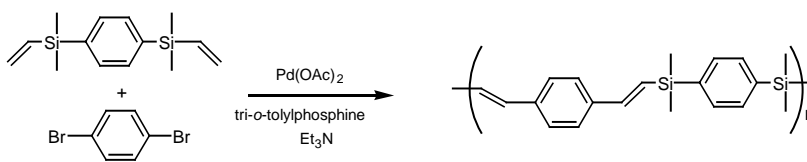


Figure 2 Absorption, excitation and emission spectra of *alt*-copoly[1,4-divinylene benzene/1,4-bis(dimethylsilylene) benzene]

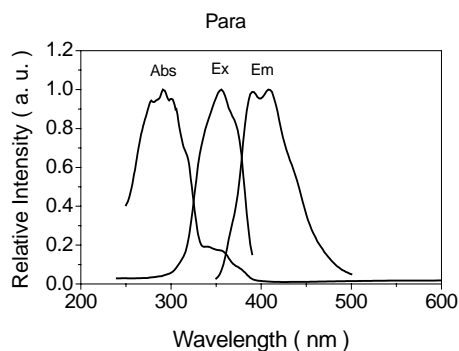
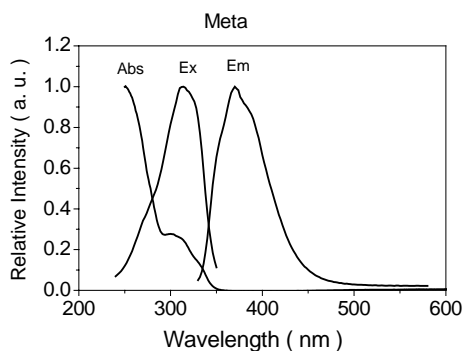


Figure 3 Absorption, excitation and emission spectra of *alt*-copoly[1,3-divinylene benzene/1,4-bis(dimethylsilylene) benzene]



Experimental

^1H , ^{13}C and ^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer. Five percent W/V chloroform-*d* solutions were used to acquire ^1H , ^{13}C and ^{29}Si NMR spectra. ^{13}C NMR spectra were obtained with broadband proton decoupling. A heteronuclear gated decoupling pulse program with a 60 s delay was used to acquire ^{29}Si NMR spectra. All spectra were referenced to internal TMS. IR spectra of neat liquid films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. Elemental analysis was carried out by Oneida Research Services, Whiteside, NY. UV spectra of CH_2Cl_2 solutions were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer. Fluorescence spectra were performed on a PTI fluorimeter. Spectra were obtained on CH_2Cl_2 solutions which had been degassed by bubbling argon for 10 min.

GPC analysis of the molecular weight distribution of the polymers was performed on a Waters system equipped with a 501 refractive index detector. Two 7.8 mm \times 300 mm Styragel HT 6E and HMW 6E columns in series with THF at a flow rate of 0.5 mL/min were used. The retention times were calibrated against known monodisperse polystyrene standards: 929000, 114 200, 13 700, 794.

1, 4-Dibromobenzene, 1, 3-diiodobenzene, palladium acetate, tri-*O*-tolylphosphine were purchased from Aldrich and used without further purification. Dimethylvinylchlorosilane was ordered from Gelest. Triethylamine and dimethylformamide were redistilled over CaH_2 and stored over 4 Å molecular sieves.

1, 4-Bis(vinyldimethylsilyl)benzene¹⁴ was prepared by the reaction of the di-Grignard reagent of 1,4-dibromobenzene with vinyldimethylchlorosilane in THF. ^1H NMR (CDCl_3 , δ ppm) 0.39 (s, 12H), 5.80 (dd, 2H, $J = 14.5$ and 2.5 Hz), 6.09 (dd, 2H, $J = 10.3$ and 2.5 Hz), 6.37 (dd, 2H, $J = 14.5$ and 10.3 Hz), 7.57 (s, 4H). ^{13}C NMR (CDCl_3 , δ ppm): -2.92, 132.75, 133.18, 137.84, 139.19. ^{29}Si NMR (CDCl_3 , δ ppm): -10.96.

alt-Copoly(1, 4-bis(dimethylsilylene)benzene/1, 4-divinylenebenzene):

A pressure tube was charged with 1, 4-bis(vinyldimethylsilyl)benzene (0.25 g, 1 mmol), 1, 4-dibromobenzene (0.24 g, 1 mmol) palladium acetate (9 mg, 0.04 mmol), tri-*O*-tolylphosphine (60.9 mg, 0.2 mmol), triethylamine (0.35 mL, 2.5 mmol), 5 mL dimethylformide and a teflon covered magnetic stirring bar. The tube was purged with nitrogen for 15 min and sealed. The reaction mixture was kept at 110 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into 50 mL methanol. The polymer precipitated and was purified by redissolving it in a minimum amount of THF and precipitating it into methanol. The resulting polymer was dried in vacuum. In this way, 0.22 g (68%) of *alt*-copoly[1,4-bis(dimethylsilylene)benzene/1,4-divinylenebenzene] ($M_w/M_n = 5400/4200$) was obtained. ^1H NMR (CDCl_3 , δ ppm) 0.41 (s, 12H), 6.55 (d, 2H, $J = 19$ Hz), 6.90 (d, 2H, $J = 19$ Hz), 7.37 (s, 4H), 7.53 (s, 4H). ^{13}C NMR (CDCl_3 , δ ppm): -2.63, 126.33, 126.69, 126.87, 127.17, 132.31, 144.77. ^{29}Si NMR (CDCl_3 , δ ppm): -10.48. IR (KBr): 3049, 2995, 2960, 2900, 1604, 1507, 1410, 1380, 1251, 1197, 1134, 1067, 1021, 988, 909, 844, 819, 735 cm^{-1} .

UV (CH₂Cl₂): $\lambda_{\max/\text{nm}}$ ϵ (L.mol⁻¹.cm⁻¹) = 355(4.4 x 10³), 315(1.44 x 10³), 301(1.95 x 10⁴), 290(1.83 x 10⁴). (C₂₀H₂₄Si₂)_n (320.58)_n: Calcd. C 74.93, H 7.54; Found C 75.23, H 7.35.

By TGA, the polymer is thermally stable to 400 °C. Above 400 °C, rapid decomposition occurs. By 600 °C, forty percent of the initial polymer sample has been lost. By 700 °C, an additional four percent weight loss occurs.

In conclusion, silicon inserted π conjugated copolymer could be produced by Heck reaction with moderate molecular weight. This silicon containing copolymer is thermally stable to 400°C, while emission of this polymer is blue-shifted, comparing with polyphenylenevinylene greenish emission. It shows potential application as organic emitter in OLED.

Acknowledgments

Ping Lu thanks the National Natural Science Foundation of China (20074032, 20374045) and Ministry of Education of China for financial support.

References

1. P. Lu, H. Hong, G. Cai, *et al.*, *J. Am. Chem. Soc.*, **2000**, *122*, 7480.
2. Z. Gao, C. S. Lee, I. Bello, *et al.*, *Appl. Phys. Lett.*, **1999**, *74*, 865.
3. G. R. Zheng, W. Li, Z. X. Wang, P. Lu, *Aust. J. Chem.* In press.
4. C. A. van Walree, M. R. Roest, W. Schuddeboom, *et al.*, *J. Am. Chem. Soc.*, **1996**, *118*, 8395.
5. H. K. Kim, M. K. Ryu, S. M. Lee, *Macromolecules*, **1997**, *30*, 1236.
6. K. L. Paik, N. S. Baek, H. K. Kim, *et al.*, *Macromolecules*, **2002**, *35*, 6782.
7. D. S. Kim, S. C. Shim, *J. Polym. Sci., Part A, Polymer Chem.*, **1999**, *37*, 2933.
8. R. M. Chen, K. M. Chien, K. T. Wong, *et al.*, *J. Am. Chem. Soc.*, **1997**, *119*, 11321.
9. R. M. Chen, T. Y. Luh, *Tetrahedron*, **1998**, *54*, 1197.
10. A. Mori, E. Takahisa, H. Kajiro, *et al.*, *Macromolecules*, **2000**, *33*, 1115.
11. M. Majchrzak, Y. Itami, B. Marciniak, *et al.*, *Tetrahedron Lett.*, **2000**, *41*, 10303.
12. Z. N. Bao, Y. N. Chen, L. P. Yu, *Macromolecules*, **1994**, *27*, 4629.
13. K. B. Wagener, D. W. Smith, *Macromolecules*, **1991**, *24*, 6073.
14. N. S. Nametkin, N. A. Pritula, T. I. Chernysheva, *et al.*, *Dokl. Nauk. SSSR*, **1965**, *164*, 1319.

Received 8 March, 2004